The present invention concerns a method of producing a shape-retaining cellulose product(s) comprising the following steps: a) providing a cellulose dispersion comprising a cellulose material and water; b) forming the cellulose dispersion to selected shape(s); c) oxidizing the cellulose dispersion with periodate; d) freezing the oxidized cellulose dispersion; e) thawing the oxidized cellulose dispersion, thereby forming a cross-linked cellulose dispersion; f) optionally performing a solvent exchange on the cross-linked cellulose dispersion; g) removing water and/or solvent from the cross-linked cellulose dispersion whilst the water and/or solvent of the dispersion is in the liquid phase, thereby providing the shape-retaining cellulose product(s), wherein step b) is performed prior to step c), simultaneously with step c) or after step c). The invention also concerns shape-retaining cellulose products obtained by such a method and uses for such products.

(54) Title: METHOD OF PRODUCING SHAPE-RETAINING CELLULOSE PRODUCTS, AND SHAPE-RETAINING CELLULOSE PRODUCTS THEREFROM

(57) Abstract: The present invention concerns a method of producing a shape-retaining cellulose product(s) comprising the following steps: a) providing a cellulose dispersion comprising a cellulose material and water; b) forming the cellulose dispersion to selected shape(s); c) oxidizing the cellulose dispersion with periodate; d) freezing the oxidized cellulose dispersion; e) thawing the oxidized cellulose dispersion, thereby forming a cross-linked cellulose dispersion; f) optionally performing a solvent exchange on the cross-linked cellulose dispersion; g) removing water and/or solvent from the cross-linked cellulose dispersion whilst the water and/or solvent of the dispersion is in the liquid phase, thereby providing the shape-retaining cellulose product(s), wherein step b) is performed prior to step c), simultaneously with step c) or after step c). The invention also concerns shape-retaining cellulose products obtained by such a method and uses for such products.
Method of producing shape-retaining cellulose products, and shape-retaining cellulose products therefrom

TECHNICAL FIELD

The present disclosure relates in general to a method of producing a shape-retaining cellulose product from a cellulosic dispersion, and the shape-retaining cellulose products obtained therefrom. The present disclosure also relates to applications for the shape-retaining cellulose products obtained.

BACKGROUND ART

Cellulose is an abundant, renewable and biodegradable material that is widely used in a variety of products, such as papers and textiles, that permeate society. However, the ability of cellulose products to maintain their given shape is often poor, especially if the cellulose product is wetted. Therefore, cellulose products are often over-dimensioned or coated in order to improve shape retention and avoid wetting.

The shape retention of cellulose products is also of relevance in the field of aerogels. Aerogels are synthetic porous ultralight materials derived from gels, wherein the liquid component of the gel has been replaced by air. They are of great interest for the production of advanced materials for use in construction, energy storage and tissue engineering, to name but a few applications.

Recently, aerogels derived from nanocellulose have gained considerable interest as an abundant, bio-derived and renewable aerogel source. However, a number of factors have hindered the widespread adoption of such nanocellulose aerogels.

Many potential applications require the formation of aerogel particles having specified shape and size distributions. However, nanocellulose aerogels are inherently friable, which limits the ability to control the shape and size distribution of aerogel particles obtained by milling of the macroscopic aerogel. Thus, applications of nanocellulose aerogels in cases where uniform aerogel shapes are required are difficult to realize with the current state of the art.
Another problem is that native nanocellulose aerogels have poor wet stability, limiting their utility and ability to be functionalized using traditional wet chemistry. In order to provide wet-stability to nanocellulose aerogels it has been necessary to add a separate chemical cross-linking agent to the nanocellulose gel, which can then be cross-linked by, for example, thermal curing.

An alternative method of crosslinking is by cryogelation, whereby a nanocellulose gel is slowly frozen to create a highly porous and wet-stable structure. However the cryogelation process has the drawback of requiring removal of the liquid from the nanocellulose gel whilst eliminating densifying capillary forces in order to avoid collapse of the aerogel structure. This can be performed either by freeze-drying (lyophilisation) of the nanocellulose gel or by critical point drying (supercritical drying), but both of these drying methods are inconvenient, require high energy inputs and specialized equipment. Moreover, an additional cross-linking step is often required after drying in order to increase wet-stability. For these reasons, the cryogelation technique is not well suited for bulk manufacturing applications, or for application to large-dimensioned cellulose products such as paper webs or textile sheets.

Jiang and Hsieh ("Super water absorbing and shape memory nanocellulose aerogels from TEMPO-oxidized cellulose nanofibrils via cyclic freezing-thawing." Journal of Materials Chemistry A 2, no. 2 (2014): 350-359) describe the synthesis of nanocellulose aerogels from TEMPO-oxidized cellulose nanofibrils (CNF) via cyclic freezing-thawing. The liquid is removed from the nanocellulose gels by freeze-drying after zero to seven freeze-thaw cycles. Prior to freezing, the aqueous CNF suspension appears as a viscous fluid, freely flowing with gravity. Only macroscopic aerogel pieces are produced.

Cai et al (Cai, Hongli, Sudhir Sharma, Wenying Liu, Wei Mu, Wei Liu, Xiaodan Zhang, and Yulin Deng. "Aerogel microspheres from natural cellulose nanofibrils and their application as cell culture scaffold." Biomacromolecules 15, no. 7 (2014): 2540-2547) describe the synthesis of microspheres of cellulose nanofibrils with polyamide-epichlorohydrin crosslinker. The microspheres are produced by spraying aqueous gel droplets into liquid nitrogen, followed by freeze-drying and then oven-curing in order to cross-link the microspheres.

Despite known solutions, there remains a need to improve the properties of cellulose products and the methods by which they are manufactured.
SUMMARY OF THE INVENTION

The inventors of the present invention have identified the shortcomings of the prior art. They have recognized that there remains a need for cellulose products that are available in any desired shape and that retain their shape, even when wetted. Moreover they have identified the need for a method of producing such shaped, shape-retaining cellulose products that is simple, efficient, readily applicable to bulk manufacturing, and applicable to all types of cellulose materials, e.g. a paper web or textile sheet.

Thus, it is an object of the present invention to provide a simple and efficient method of producing shape-retaining cellulose products that allows for a great variety of shapes to be produced in any desired size, including large scale, that is applicable to all types of cellulose materials, and that is readily applicable to bulk manufacturing.

It is a further object of the present invention to provide shape-retaining cellulose products that are produced to any desired shape and size, and that return to their original shape after deformation, even when wetted.

According to one aspect of the present invention, these objects are achieved by a method of producing a shape-retaining cellulose product(s) according to the appended claims. The method comprises the following steps:

a) providing a cellulose dispersion comprising a cellulose material and water;
b) forming the cellulose dispersion to selected shape(s);
c) oxidizing the cellulose dispersion with periodate;
d) freezing the oxidized cellulose dispersion;
e) thawing the oxidized cellulose dispersion, thereby forming a cross-linked cellulose dispersion;
f) optionally performing a solvent exchange on the cross-linked cellulose dispersion;
g) removing water and/or solvent from the cross-linked cellulose dispersion whilst the water and/or solvent of the dispersion is in the liquid phase, thereby providing the shape-retaining cellulose product(s),

wherein step b) is performed prior to step c), simultaneously with step c) or after step c).
Oxidizing the cellulose dispersion using periodate has the dual effect of furnishing the cellulose with dialdehyde moieties and allowing the compaction of the cellulose, presumably due to the scission of the C2-C3 bond in the repeating anhydroglucose units of the cellulose. Freezing and thawing of this oxidized cellulose dispersion creates a highly cross-linked cellulose dispersion. This highly cross-linked dispersion is sufficiently stable so that water and/or solvent can be removed from the dispersion in the liquid phase, without risking collapse of the structure due to capillary forces. Therefore, freeze-drying or supercritical drying is not required, and the cellulose product can be dried using conventional means. The obtained cellulose product retains the shape that it was formed in, even under wet conditions.

If temporarily deformed by stretching or compression, the cellulose product returns to its original shape afterwards.

In the drying step g), the water and/or solvent may be removed by pressing, filtration, evaporation, or combinations thereof. Thus, conventional drying means already widely used in the paper and textile industries can be used for drying to give the shape-retaining cellulose product without destroying the formed shape.

In step b) of forming the cellulose dispersion to selected shapes, this step may be performed by a method selected from extrusion, printing, 3D-printing, molding, embossing, emulsifying and deposition on a hydrophobic surface. Thus, a wide variety of common forming methods can be used in conjunction with the present method, and cellulose dispersions having a wide range of rheological properties can be formed by selection of an appropriate forming technique.

If step b) is performed prior to step c) then the formed cellulose dispersion shapes may be placed in an aqueous periodate bath. The periodate bath may suitably have a periodate concentration of from about 0.5 to about 10 percent by weight. This is a simple and convenient method of oxidizing already-formed shapes.

If step b) is performed simultaneously with step c) or after step c) then the periodate may be blended as a powder or aqueous solution into the cellulose dispersion. The cellulose dispersion after blending may suitably have a periodate concentration of from about 0.5 to about 10 percent, defined as dry weight periodate relative to the total weight of the cellulose dispersion. This is a simple method of ensuring that the entirety of the formed cellulose
dispersion shape is subject to oxidation by the periodate, without having to consider the diffusion rate of the periodate.

The method of the present invention may comprise an additional step h) after step c), wherein step h) comprises providing a particulate material and blending the particulate material with the oxidized cellulose dispersion, thereby providing a composite dispersion. In this case, the particulate material may suitably be added in a quantity of from about 1 to about 80 percent, preferably from about 1 to about 60 percent, defined as the dry weight of the particulate material relative to the total dry weight of the composite dispersion. The particulate material may be selected from wood pulp, sawdust, ground wood, ground bark, wood fibre, rosin, polymers, polylactic acid, metals, powdered minerals, pigments, graphene, graphite, nanoparticles, nanotubes, and/or combinations thereof. In this manner, composite nanocellulose products possessing a wide variety of properties, such as for example electrical conductivity, may be obtained.

The method of the present invention is applicable using a wide variety of cellulose materials as feedstock.

The cellulose material of the cellulose dispersion may be nanocellulose. In this case, the cellulose dispersion may suitably comprise from about 0.4 to about 10 percent of nanocellulose, defined as dry weight nanocellulose relative to the total weight of the cellulose dispersion. By using nanocellulose as the cellulose material, formable, shape-retaining nanocellulose aerogel shapes are obtained. The nanocellulose may be wood- or plant-based and is chosen from cellulose nanofibrils (CNF) or cellulose nanocrystals (CNC), preferably cellulose nanofibrils. This ensures that the raw materials for the cellulose product are obtained from an abundant, renewable and biodegradable source.

The cellulose material of the cellulose dispersion may be wood fiber, paper pulp, regenerated cellulose, cotton, linen, abaca, coir, flax, henequen, kenaf, jute, hemp, kapok, raffia, ramie, bamboo, pina, sisal, or combinations thereof. In this case, the cellulose dispersion may suitably comprise from about 15 to about 90 percent of cellulose material, defined as dry weight cellulose material relative to the total weight of the cellulose dispersion. By using these materials as the cellulose material, shape-retaining paper and textile products are obtained that can replace petrochemical-derived products such as plastics in a variety of applications.
The cellulose material of the cellulose dispersion may be microcrystalline cellulose, carboxymethyl cellulose, cellulose gels, or combinations thereof. In this case, the cellulose dispersion may suitably comprise from about 0.4 to about 10 percent of cellulose material, defined as dry weight cellulose material relative to the total weight of the cellulose dispersion.

According to a further aspect of the present invention, the objects of the present invention are achieved by a shape-retaining cellulose product obtained by the inventive method described. Cellulose products obtained by the inventive method retain the shape that they are formed in, even under wet conditions. If temporarily deformed by stretching or compression, the cellulose products return to their original shape afterwards.

Nanocellulose aerogel shapes may be obtained by the inventive method if the cellulosic material feedstock is nanocellulose. Nanocellulose aerogels produced by the inventive method can be provided in any shape, have high shape retention and excellent wet stability.

Nanocellulose aerogel shapes obtained by the inventive method may have a variety of applications, including use as paper additives, in the manufacture of textiles, in energy storage applications, or as a chromatography or filtration media in the purification of liquids or gases. Thus, a large variety of advanced materials may be obtained using the nanocellulose aerogel shapes.

Shape-retaining papers may be obtained by the present method. Such shape-retaining papers may be used as a green alternative to, for example, petrochemical-derived polymers in a number of applications.

Shape-retaining textiles may be obtained by the present method. Such shape-retaining textiles may be used as a green alternative to, for example, wrinkle-resistant or non-iron treatments for clothing garments.

Further aspects, objects and advantages are defined in the detailed description below.

DETAILED DESCRIPTION

The cellulose material for use in the present invention may be any cellulose material known in the art, such as nanocellulose, wood fiber, paper pulp, regenerated cellulose (e.g. rayon, acetate, modal and lyocell), cotton, linen, abaca, coir, flax, henequen, kenaf, jute, hemp,
kapok, raffia, ramie, bamboo, pina, sisal, microcrystalline cellulose, carboxymethyl cellulose or other cellulose gels. The cellulose material comprises about 40 weight percent or more cellulose by dry weight, preferably 80 weight percent or more.

Nanocellulose is further known as microfibrillated cellulose (MFC), nanofibrillated cellulose (NFC), cellulose nanofibrils (CNF) and cellulose nanocrystals (CNC). CNF is the preferred from of nanocellulose in the present invention. By nanocellulose it is meant cellulose fibre derived material that is produced through a nanofibrillation process, whereby the fibre wall is disintegrated into a major fraction of individualized elementary nanofibrils and their aggregates. Various enzymatic and/or chemical pretreatments of the cellulosic material can facilitate the fibrillation process. Nanofibrils have diameters of roughly 5-100 nm and can have lengths up to several micrometers. The nanocellulose is preferably wood- or plant-based.

Suitable paper pulps for use as the cellulose material include, but are not limited to, kraft, soda, sulfite, mechanical, a thermomechanical (TMP), a semi-chemical, or a chemi-thermomechanical (CTMP) pulps. A raw material for the pulps can be based on softwood, hardwood, recycled fibres or non-wood fibres. The softwood tree species can be for example, but are not limited to: spruce, pine, fir, larch, cedar, and hemlock. Examples of hardwood species from which pulp useful as a starting material in the present invention can be derived include, but are not limited to: birch, oak, poplar, beech, eucalyptus, acacia, maple, alder, aspen, gum trees and gmelina. The raw material may comprise a mixture of different softwoods, e.g. pine and spruce. The raw material may also comprise a non-wood raw material, such as bamboo, sugar beet pulp, wheat straw, soy hulls and bagasse. The raw material may also be a mixture of at least two of softwood, hardwood and/or non-wood.

Since cellulose material can be produced from various green resources, such as wood, agricultural residues and annual crops, it is thus abundant, renewable and biodegradable.

Method

The method of the present invention comprises the following steps. The steps are performed in alphabetical order unless otherwise specified.

a) Providing a cellulose dispersion comprising a cellulose material and water.
The cellulose dispersion is provided as a dispersion comprising from about 0.4 to about 90 percent of cellulose material, defined as dry weight cellulose material relative to the total weight of the cellulose dispersion. Depending on the content of cellulose material, the cellulose dispersion may therefore be characterised as cellulose dispersed in an aqueous continuous phase, or as water dispersed in a cellulose continuous phase such as in a water-swelled fiber. The optimal cellulose content of the cellulose dispersion depends on a number of factors, including the cellulose material being used, and the forming technique to be applied.

The cellulose dispersion may preferably comprise from about 0.4 to about 10 percent of cellulose material, defined as dry weight cellulose material relative to the total weight of the cellulose dispersion, when the cellulose material is nanocellulose, microcrystalline cellulose, carboxymethyl cellulose, cellulose gels, or combinations thereof.

The cellulose dispersion may preferably comprise from about 15 to about 90 percent of cellulose material, defined as dry weight cellulose material relative to the total weight of the cellulose dispersion, when the cellulose material is wood fiber, paper pulp, regenerated cellulose, cotton, linen, abaca, coir, flax, henequen, kenaf, jute, hemp, kapok, raffia, ramie, bamboo, pina, sisal, or combinations thereof.

The cellulose dispersion may essentially consist only of cellulose material and water. However, the cellulose dispersion may also comprise further additives, for instance in order to adapt the dispersion viscosity and/or freezing rate. Such additives may include salts, pH adjusting agents and/or co-solvents such as alcohols. Thus, the cellulose dispersion may essentially consist only of cellulose material, water, solvent(s) and salt(s).

b) Forming the cellulose dispersion to selected shape(s).

By shapes is meant the physical form or contour of the formed cellulose dispersion produced.

Common shapes in the present context include spherical particles, beads, fibers having a circular or otherwise shaped cross-section, alphanumerical characters, currency symbol characters, and any characters represented by the Unicode standard. Further shapes may be fibers or sheets having micro-wrinkles, waves, crepe, kinks, undulations, flat (compressed) fibrous webs, and 3D shapes. However, any conceivable 1-, 2- and 3D-shape may be produced.
The shapes produced may have dimensions within the range from about 100 nm to about 5 m, such as from about 1 µm to about 20 mm, such as from about 1 µm to about 8 mm. If a shape is discrete, such as a particle, bead or character, it may have all three dimensions within the range from about 100 nm to about 8 mm, whereas if it is elongated or continuous, such as a fiber or sheet, then it may be desirable to have a larger size in one or two dimensions. Fibers and sheets can be formed as continuous or to a selected length.

Techniques that may be used for forming the cellulose dispersion include extrusion, printing, 3D-printing, molding, embossing, emulsifying and deposition of droplets on a hydrophobic surface. These techniques can be performed using standard equipment as known in the art. The cellulose dispersion is adapted to have rheological properties suitable for the technique chosen. The cellulose dispersion may be formed prior to oxidation by periodate, as this is advantageous in some cases. However, the nanocellulose dispersion may also be formed at a time after adding periodate to the nanocellulose dispersion, i.e. whilst the oxidation is ongoing or completed.

c) The cellulose dispersion is oxidized with periodate either prior to, simultaneously with, or after forming shapes. By periodate it is meant any chemical compound including a periodate moiety. The periodate moiety can be a metaperiodate or an orthoperiodate. Such compounds include sodium periodate, potassium periodate and periodic acid. Sodium metaperiodate is preferred. Oxidation by periodate oxidatively cleaves the C2-C3 glycolic moiety in the cellulose anhydroglucose repeating units to a dialdehyde moiety. A suitable degree of oxidation may be from about 5 to about 50 percent, as determined by reaction with hydroxylamine followed by sodium hydroxide titration.

If the oxidation is to take place prior to, or simultaneously with shape forming, the periodate may be blended into the cellulose dispersion, either as a solid or in solution. A suitable periodate concentration in this case may be from about 0.5 to about 10 percent, defined as dry weight periodate relative to the total weight of the cellulose dispersion. If the oxidation is performed after forming shapes, the formed shapes may be soaked in a periodate bath for a specified period of time until a desired degree of oxidation is obtained. The periodate bath may suitably have a periodate concentration of from about 0.5 to about 10 percent by weight.
The oxidation may suitably be performed at any temperature above the melting point of water (0 °C at ambient pressure) and below the boiling point of water (100 °C at ambient pressure). However, at temperatures higher than 40 °C discoloration may result, presumably due to side reactions occurring. Therefore, an optimal balance between reaction rate and selectivity is obtained by performing the oxidation at from about 10 °C to about 40 °C, or preferably from about 20 °C to 30 °C. The oxidation may for example be performed for a duration of from about 30 minutes to about 48 hours, but is not limited to this range.

During oxidation, the cellulose dispersion shapes may shrink isotropically by as much as 50%. Without wishing to be bound by theory, this may be due to the structural compaction of the gel during oxidation due to the increased flexibility induced to the fibrils by the opening of the repeating anhydroglucose units.

d) After oxidation, the cellulose dispersion is frozen.

The cellulose dispersion may be frozen at any temperature from -1 °C to -200 °C. Freezing at moderate temperatures of 0 °C to -50 °C provides cross-linked cellulose dispersions that are stronger and have greater wet stability, but adequate strength and wet stability is obtained even at lower freezing temperatures, such as from -70 °C to -200 °C. For example, cellulose dispersion shapes frozen by immersion into a liquid nitrogen bath (-196 °C) have adequate mechanical- and wet-stability upon thawing, meaning that it is possible to perform the freezing step in a rapid and efficient manner using liquid nitrogen. The duration of the freezing step can be readily determined by the skilled person and depends on the freezing temperature and the dimensions of the substrate. However, freezing times of from about 30 seconds to about 48 hours may be applicable.

e) After freezing, the cellulose dispersion is then thawed to complete the cross-linking of the cellulose dispersion.

When thawing, the frozen cellulose dispersion can be brought to any temperature above the melting point of water (0 °C at ambient pressure) and below the boiling point of water (100 °C at ambient pressure). However, excessively high temperatures lead to decomposition or side-reactions from any remaining periodate, and therefore temperatures of from about +1 °C to about 40 °C are often suitable. Depending on the time provided for oxidation in step c), the
oxidation reaction may not have proceeded to completion and further oxidation and cross-linking of the cellulose may occur during the thawing stage. The thawed, cross-linked cellulose dispersion can be maintained at the thawing temperature for from about 30 minutes to about 48 hours.

The cellulose dispersion may be subjected to only a single freeze-thaw cycle. A single freeze-thaw cycle is sufficient to provide a cellulose product with adequate strength, wet stability and shape-retention after drying. However, these properties may in some cases be improved by performing multiple freeze-thaw cycles. The mechanical integrity of the cross-linked cellulose dispersion may be further increased in some cases by performing a subsequent additional oxidation step and freeze-thaw cycle after the initial freeze-thaw cycle.

Without wishing to be bound by theory, the cross-linking of the cellulose dispersion is considered to proceed via hemiacetal bond formation between hydroxyl groups of the nanocellulose and aldehyde moieties introduced by periodate-induced oxidative cleavage of the C2-C3 bond of the repeating anhydroglucose units in the nanocellulose. Judging by the shape-retention, mechanical integrity and wet strength of the final nanocellulose aerogel products, the hemiacetal bonds formed are both abundant and resilient. This is unexpected, since in aqueous solution the equilibrium of "free" hemiacetals is strongly shifted towards the corresponding alcohol and aldehyde.

f) After performing the freeze-linking stage, the cross-linked cellulose dispersion may be washed in order to remove unreacted reagent, reaction byproducts and excess cellulose not forming part of the cross-linked cellulose network. This can be performed, for example, by exchanging the liquid phase of the dispersion a number of times, with a suitable incubation time between each exchange. The exchange may be performed using water only, or may be performed using one or several organic solvents. Suitable solvents include, but are not limited to, acetone, methanol, ethanol, propanol, butanol, THF and 1,4-dioxane. For example, the liquid phase of the nanocellulose gel may first be exchanged using ethanol multiple times, e.g. 1-5 times, followed by exchange using acetone multiple times, e.g. 1-5 times.

g) The cross-linked cellulose dispersions are then dried by removing water and/or solvent.
Due to the extensive cross-linking obtained by periodate oxidation and freeze-linking, the cellulosic dispersions can withstand densifying capillary forces during drying without collapsing, and the dispersions can therefore be dried while the liquid component of the dispersion is in the liquid phase. Therefore, conventional drying means such as filtration and evaporation may be utilized. The cross-linked cellulose dispersions have outstanding mechanical integrity so that liquid may even be removed by pressing the formed cellulose shapes. Upon release of the pressure, the cellulose shapes return to their original shape.

The cross-linked cellulose dispersions need not be subjected to freeze-drying or supercritical drying. Being able to dry the gels by conventional means such as pressing, filtration and evaporation, as compared to freeze-drying or supercritical drying, is a significant advantage, especially in bulk applications such as for paper and textile applications. Upon drying, the dimensions of the cellulose shape may contract somewhat, but the main shrinkage in dimension takes place during the oxidation stage.

The cross-linked cellulose shapes may be dried in isolation, or they may be added to a further material prior to drying step g). As a non-limiting example, cross-linked cellulose shapes may be added to a paper production process at any stage prior to the drying section of the papermaking process; e.g. added to the paperstock or added in the forming section of the papermaking machine. These cross-linked cellulose shapes will then be dried together with the paper in the press section and/or dryer section of the papermaking machine.

Pure shape-retaining cellulose products may be obtained by using only the steps a) to g) above. However, an additional step h) may be included, wherein the oxidized cellulose dispersion from step c) may be blended with a particulate material prior to forming step b), thereby providing a composite dispersion. By particulate material it is meant any material that is solid at the processing temperature (commonly between about 0 and 50 °C) is non-soluble in the cellulose dispersion, and is of a suitable size for inclusion into the cellulose dispersion. By suitable size it is meant from about 1 nm to about 10 mm, preferably from about 1 mm to about 1 mm, even more preferably from about 1 mm to about 500 µm. The particulate material may for example be in the form of powder, beads or fibers. A non-exhaustive list of particulate materials suitable for inclusion in the composite dispersion includes wood pulp, sawdust, ground wood, ground bark, wood fibre, rosin, polymers (e.g. polylactic acid), metals (e.g. iron,
copper, brass, bronze), minerals (e.g. marble, gypsum), pigments, graphene, graphite, nanoparticles, nanotubes, and/or combinations thereof. The particulate material may be added in a quantity of from about 1 to about 80 percent, preferably from about 1 to about 60 percent, defined as the dry weight of the particulate material relative to the total dry weight of the composite dispersion. After blending the cellulose dispersion with the particulate material thereby obtaining the composite dispersion, the composite dispersion is formed, freeze-thawed, optionally solvent-exchanged, and dried as described in steps b), d) e) and f) above.

The cellulose of the shape-retaining cellulose product may be functionalized in a functionalization step j). This functionalization step j) may be performed after the drying step g). However, the cross-linked cellulose dispersion obtained after step e) has adequate mechanical integrity to allow a functionalization step to be performed after step e) but prior to step g). This allows a functionalization to be performed prior to drying and therefore eliminates the need for a multiple drying steps. Functionalization can be performed using any technique known in the art, such as the layer-by-layer technique, esterification, alkylation, caboxyalkylation and hydroxyalkylation.

Products

All cellulose products obtained by the present method display a high degree of shape retention, even upon wetting. If deformed, for example by stretching or compressing, the cellulose products retain their original shape upon cessation of the deforming force.

Aerogels

If nanocellulose is used as the cellulose material in the method described above, nanocellulose aerogel shapes are obtained. Such a method provides a simple and efficient means of producing wet-stable nanocellulose aerogel shapes; that allows for a great variety of shapes to be produced in a desired size, without the need for an expensive drying stage or an additional crosslinking agent.

By aerogel it is meant a synthetic porous ultralight material derived from a gel, wherein the liquid component of the gel has been replaced by a gas. This definition also encompasses xerogels, where the liquid component of the gel has been removed by evaporation. The
aerogels of the present application are prepared by removing water and/or solvent from the nanocellulose gel whilst the water and/or solvent of the nanocellulose gel is in the liquid phase.

The nanocellulose aerogels produced by the method described above have a great mechanical integrity, are elastically deformable, and have high wet-stability. This means that after production, the aerogel shapes can be deformed by compression or stretching, and will return to their original shape upon cessation of the deforming force, regardless of whether they are dry or wetted. This means that they can readily be functionalized using conventional wet chemistry techniques. Their shape can be controlled to a high degree of precision. For example, essentially spherical aerogel particles of a selected diameter may be formed. Composite nanocellulose aerogels may readily be formed by adding particulate material to the nanocellulose dispersion as described above.

These properties mean that aerogels produced by the method described above readily lend themselves to a number of applications.

The nanocellulose aerogel shapes can be used as paper additives. Nanocellulose aerogels produced by the present method are especially suitable for use in paper applications due to their high wet stability even prior to drying, meaning the still-wet shapes obtained after freeze-linking may be dewatered and dried together with the paper pulp in the papermaking process. For example, the still-wet shapes may be mixed with the paperstock or may be added in the forming section of the papermaking machine. Nanocellulose aerogel shapes may be added to paper in order to increase bulk, provide thermal insulation properties, improve elasticity, increase impact resistance, or increase the specific surface area of the paper. Specially shaped aerogels may be produced and added to security paper as a tactile and/or visual anti-counterfeiting feature.

The same benefits can be obtained when using the nanocellulose aerogel shapes of the present invention as additives in the manufacture of textiles, for instance, as additives to regenerated cellulose textiles.
Nanocellulose dispersions may be used as ink in 2-D and 3-D printing. The formed shapes, upon freeze-thawing and drying, have high shape retention and are readily functionalized, making them suitable as scaffolds in tissue engineering applications.

Nanocellulose aerogel particles may be used as a component in a functional ink, dispersed in a printing vehicle and deposited by e.g. stencil or screen printing in order to form printed functional components. For printing applications, such as screen-printing of electronic components, a polydisperse size distribution with particles in the range of from about 500 nm to about 200 μm, or preferably from about 1 μm to about 50 μm, may be appropriate. The particles are preferably spherical since this limits entanglements between ink particles and optimizes the ink flow to the substrate. The particle size may for example be tailored to avoid the printed particles being able to enter a porous substrate such as paper. As a printing vehicle, solvents, aqueous solutions, polyelectrolytes or non-aqueous ionic solvents such as e.g. ionic liquids may be used. Thus, for example, printed components for batteries or capacitors, such as separators, electrodes or plates, may be printed.

Composite aerogel shapes comprising electrically-conducting particulate material can be produced. These can be used as materials in energy storage applications, for example in supercapacitors, semi-solid flow batteries and polymer batteries. The ability to 3D-print using an electrically-conducting composite nanocellulose dispersion means that battery components such as electrodes can be printed to the specified size and shape, thus minimizing material wastage.

Composite aerogel shapes comprising dielectric particulate material can be produced, having a controlled pore size, porosity, thickness and wet-stability. These can be used, for example, as separators in batteries. Such separators could be 3D-printed using a dielectric nanocellulose composite dispersion as ink, thus minimizing material wastage.

Functionalized nanocellulose aerogel beads, or alternatively, nanocellulose composite beads, could be used as a porous chromatography or filtration media for the purification of fluids such as water or air.

*Paper*
If paper pulp is used as the cellulose material in the method described above, shape-retaining paper is obtained. The obtained paper also has superior shape retention when wet, as well as good wet strength. The entire paper web may be treated according to the method above, or only specific parts of the web where shape-retention is of greater importance, e.g. folds. Paper may be provided with a permanent shape such as folds, creases, pleats or creping.

Paper produced by the method above is especially suitable for producing creep-resistant paper, especially paper resistant to mechanic-sorptive creep. Such creep-resistant paper is useful in, for example, packaging applications, construction applications, and other applications where the paper may be subjected to moisture variations.

Elastic papers may also be produced by the method above, which may find application in a wide variety of areas.

**Textiles**

If regenerated cellulose, linen, abaca, coir, flax, henequen, kenaf, jute, hemp, kapok, raffia, ramie, bamboo, piña, sisal, or cotton is used as the cellulose material in the method described above, shape-retaining textiles are obtained. Such textiles may be produced having properties such as permanent creasing, non-crease (self-flattening), creping, crimping, or pleating. If the textile is temporarily deformed from the given shape, it will return to the shape upon the cessation of the deforming force.

**Examples**

CNFs with a charge density of 600 μeq/g were provided by Innventia AB, Stockholm, Sweden as a 2 wt% aqueous dispersion prepared and characterized according to procedures described in: Wagberg, L., G. Decher, M. Norgren, T. Lindstrom, M. Ankerfors, and K. Axnas, The Build-U p of Polyelectrolyte Multi layers of Microfibrillated Cellulose and Cationic Polyelectrolytes. Langmuir, 2008. 24(3): p. 784-795. Solid alkyl ketene dimer (AKD) was supplied by EKA Chemicals, Bohus, Sweden. Sodium meta periodate was purchased from Alfa Aesar GmbH Co KB (Karlsruhe, Germany). Branched polyethylene meline (PEI) with a molecular weight of 60 kDa was purchased as a 50 wt% aqueous solution from Arcos Organics (U.S). Sodium poly[2-(3-tienyl)ethoxy-4-butyl-sulfonate] (SPTBS) was acquired as a dry powder from American Dye Source Inc. (Montreal, QC, Canada). Stable dispersions were produced from single-walled
carbon nanotubes (CF-SWCNTs) functionalized with carboxyl groups purchased from Carbon Solutions Inc (Riverside, CA, USA). All chemicals were used without further purification unless otherwise stated. MilliQ water was used throughout.

Example 1: Synthesis of spherical nanocellulose aerogel beads

Spherical particles were formed by placing CNF gel droplets on a superhydrophobic AKD surface produced by a Rapid Expansion from a Supercritical Solution (RESS) method. The CNF droplets were subsequently frozen, thawed, solvent-exchanged and dried to form the aerogel beads according to the following more detailed description.

A superhydrophobic AKD surface was used to ensure that the beads were as spherical as possible. This surface was produced by the following RESS method. About 2 g of AKD was placed in the spraying apparatus, the operating pressure was set to 25 MPa and the pre-heating stage, cell and nozzle temperatures were set to 70 °C, 70 °C and 90 °C respectively. After filling and pressurizing the pump with CO2, the valves were opened and when steady-state operating conditions had been reached a microscope slide was moved perpendicular to the nozzle at a distance of 30 mm. The total spraying volume was 70 mL. After spray deposition, the surface was transferred to and stored in a sealed petri-dish until further use.

In order to prepare the nanocellulose aerogel bead, sodium metaperiodate was added to a 2 wt% CNF gel and mixed thoroughly with an Ultra Turrax (IKA 115 Werke GmbH & Co. KG, Staufen, Germany) at 10 000 rpm for 5 min. The mixture was diluted with Milli-Q water and agitated vigorously to a low viscous CNF dispersion with a final CNF consistency of 1.4 wt% and a periodate concentration of 0.057 M. The periodate-containing CNF dispersion was transferred to a plastic syringe equipped with a 21G stainless steel needle with the sharp part cut off. Droplets of the periodate-containing CNF dispersion, with diameters <2.7 mm were then deposited on the superhydrophobic surface by hand. To prevent water from evaporating from the droplets, a lid was placed over the superhydrophobic surface. To further limit evaporation, a beaker containing hot water was placed under the lid. The whole set-up was then covered with aluminium foil to prevent exposure to light, and the CNFs were oxidized for 20 h, after which the beads formed were removed from the superhydrophobic surface, placed individually on a polystyrene surface and subsequently frozen at -18 °C for 2 h. The beads were thereafter completely thawed, without drying, at room temperature before being
solvent-exchanged, first to 96% ethanol and then to acetone. Both solvents were changed three times with an incubation time of 15 min between each solvent change. After solvent-exchange, the beads were collected by filtering off the acetone through a stainless steel mesh and completely dried in air while still resting on the mesh.

The final nanocellulose aerogel beads contained 2.1 mmol/g aldehyde corresponding to a degree of oxidation of about 18% and had a total charge of 300 μeq/g. The oxidation of the CNFs was shown by a characteristic peak appearing at 1730 cm⁻¹ in the FTIR-spectra of the pristine aerogel beads. The beads were spherical with an average weight of 0.08 mg and an average diameter of 1.8 ± 0.2 mm. The drying procedure had no significant impact on the sphere diameter, which suggests that a strong CNF network is formed that can resist the capillary forces and prevent a collapse of the structure during drying. The aerogel beads had a (individual aerogel sphere) density of 24.5 kg/m³ and a porosity of 98%. The pores within the aerogel beads appear to be interconnected. This was supported by the fact that the beads did not float in water but were completely filled with water when completely submerged, resting on the bottom of the container. The beads had excellent shape-recovery properties and aerogel beads soaked for four days did not display any major reduction in their shape-recovery capacity as compared to beads soaked for only 30 minutes. This suggests that the nanocellulose aerogel bead structure is held together strongly and that the chemical cross-links are retained to a substantial extent even after four days in water.

Example 2: 3D-printing of nanocellulose aerogel shapes

Ring structures of 1.4% (w/w) CNF gel, having a diameter of 5 mm, were 3D printed on a Mylar film in an Ultimaker2 3D printer with a syringe nozzle of 0.65 mm. The ring structures were soaked in solutions of sodium periodate, with a concentration of 1%, 2%, 5% and 10% respectively, then oxidized at room temperature in darkness for 24 hours and finally frozen (-20 °C), thawed and dried. The resulting shrinkage of the CNF rings was proportional to the sodium periodate concentration. The best results in terms of shape consistency and mechanical properties was obtained at 2% and 5% sodium periodate concentration.

Example 3: Formation of polydisperse nanocellulose aerogel microspheres
A mixture of 15.5 g CNF gel (1.8 % (w/w), exfoliated by 4 passes through a homogenizer), 4.5 g water and 0.28 g sodium periodate, was mixed at 20500 rpm during 5 minutes in an Ultra-Turrax T25. A blend of said mixture (4 g) and castor oil (36 g), was first obtained by hand blending followed by emulsification in a rotational rheometer, RheolabQC, Anton Paar with measuring geometry CC39 at constant speed (1200 1/min) during 120 seconds.

The resulting emulsion was poured into aluminum molds (diameter 7.5 cm) in a thin layer and immediately frozen at -20 °C or in liquid nitrogen (-196 °C) and kept in a frozen state overnight.

After thawing, the emulsions were kept in the dark (to reduce side reactions) during 24 hours at room temperature or at +40°C. The removal of the castor oil and drying by solvent exchange was performed in three steps: First the emulsions were stirred with an excess of ethanol for 10 minutes and then filtered on a nylon wire filter. Then the resulting CNF particles were washed with ethanol, and finally washed with acetone. The particles were then left to dry on the nylon wire filter.

The resulting nanocellulose aerogel spheres were polydisperse and had a particle diameter in the range from about 1 to about 50 \( \mu \text{m} \).

The aerogel spheres obtained were dispersed in water and used in stencil and screen printing. Using this technique, a separator could be printed between two conductive surfaces (carbon black printed PET films). The printing was successful and no electrical short was obtained through the printed separator.

**Example 4: Dewatering moulded nanocellulose aerogel shapes by pressing**

A mixture of 15.5 g carboxymethylated CNF gel (1.8 % (w/w) exfoliated by 4 passes through a homogenizer), 4.5 g water and 0.28 g sodium periodate was mixed at 20500 rpm during 5 minutes in an Ultra-Turrax T25. 8 mL was then poured into plastic moulds (diameter 3 cm) and immediately frozen (-20 °C) and kept in a frozen state overnight. After thawing, the gel structure was kept at ambient temperature in the dark during 24 hours and the shrunken gel structure was then removed from the surrounding free water solution. The gel structure could be pressed using the index finger, resulting in that the majority of the water was squeezed out while the gel was kept in one piece. The original shape was retained upon the cessation of
pressure on the gel structure. If the pressed-out water was not removed by soaking in a blotting paper or a press felt, it was re-adsorbed by the gel when the original shape was retained.

Example 5: Functionalization of Nanocellulose Aerogel Beads

The beads obtained in Example 1 were functionalized using a layer-by-layer technique. The spherical aerogel beads were functionalized with two different systems; SWCNT/PEI and SPTBS/PEI. For the SWCNT/PEI system, the concentrations of both species were 0.2 g/L, and for the SPTBS/PEI system the concentrations were 1 g/L. The pH of the PEI solution was adjusted to 10 by addition of sodium hydroxide solution and the pH of the SPTBS solution was adjusted to 4 by addition of hydrochloric acid.

Prior to functionalization the beads were washed by repeated soaking and dewatering until the conductivity of the washing water was below 5 μS/cm. The LbL procedure was then performed by alternately adding cationic PEI and anionic CF-SWCNTs or SPTBS to the vial containing the wet beads and allowing adsorption to take place for 5 min. To make sure that the beads were completely covered by the liquid, a plastic rod was used to push them to the bottom of the vial. The rest of the adsorption was carried out under continuous mild shaking of the vial on a shaking table. After 5 min, the non-adsorbed polyelectrolytes/nanoparticles were separated from the beads by filtration. Between each adsorbed layer, the beads were washed four times with 40 mL of water to remove polyelectrolyte/nanoparticles still remaining inside the beads.

The high specific surface area of the cross-linked aerogel beads in combination with their fairly high surface charge, 300 μeq/g, make them excellent templates for surface functionalization using the LbL-technique with charged polymers and nanoparticles. The functionalization by LbL formation of multilayers within the aerogel beads was successful and both the anionic and cationic components displayed linear growth behaviour when assembled into multilayers. The growth per layer was calculated to be 23.2 and 19.6 mg/g for SPTBS and CF-SWCNTs, respectively, which corresponds to a total adsorbed amount of 116 mg/g and 98 mg/g in 5 bilayers.
Example 6: Conducting nanocellulose / carbon nanotube composites

Carboxyl-functionalized single-walled carbon nanotube dispersion was stirred into a carboxymethylated CNF dispersion while adding MilliQ water and sodium metaperiodate to arrive at a total concentration of 1.4% CNF. The added weight of the CNTs was 1.8 % of the total solid content of CNFs, and the total concentration of periodate was 0.057 M. The mixture was further oxidized by covering with aluminium foil to prevent exposure to light, and leaving to react at room temperature, overnight. The sample, contained in a 2.5 cm diameter cylinder, was subsequently frozen at -18 °C for 2 hours, thawed to room temperature and dried by solvent exchange. The obtained resistance of the CNT:CNF aerogel (180 kOhm) is comparable to the addition of 5 bilayers of CNTs and PEI to a pure freeze linked CNF aerogel.

Example 7: Composite nanocellulose aerogels

1.8% (w/w) CNF gel was mixed with sodium periodate to a concentration of 0.057 M. Various fillers were added to a total particulate material concentration of 1%, 3%, 10% or 50%. The composite mixture was put in a cylindrical dish (diameter 2.5cm) oxidized for 2 hours at room temperature in a dark environment, frozen at -18 degrees Celcius for 2 hours, thawed to room temperature, and later dried by solvent exchange, filtration and atmospheric evaporation. The composite aerogels formed are shown in Table 1, together with the degree of shrinkage observed in the final product.

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<th>Particulate material</th>
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<td>CNF only (no particulate mate rial)</td>
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<tr>
<td>Gypsum 50%</td>
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<td>Gypsum 10%</td>
<td>8%</td>
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<td>Brass powder 10%</td>
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<td>Brass powder 1%</td>
<td>22%</td>
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</table>
Other fillers were tested as well including: saw dust, corn starch, cement, sorbitol, bark, lignin powder and kolofonium. Stable composite nanocellulose aerogel materials could be formed using all of the materials tested at all particulate material concentrations tested. It can be seen that the choice of particulate material affects the degree of shrinkage of the composite aerogel.

Example 8: Shape-retaining lyocellfibers

A bundle of regenerated Lyocell rayon fibres were spiralled and fixed around a one centimeter diameter glass rod. The fibres were then swelled and oxidized in MilliQ water mixed with 0.057 M sodium periodate for 1 hour in room temperature in a dark environment. Freezing for 2 hours at -20 °C and thawing resulted in the rayon fibre bundles being crosslinked and fixed in the spiral shape. The fibers were subsequently dried by solvent exchange and filtration. The resulting lyocell spiral retains its shape and is elastic in the radial directing (relative to the central longitudinal axis of the spiral).
CLAIMS

1. Method of producing a shape-retaining cellulose product(s) comprising the following steps:
   a) providing a cellulose dispersion comprising a cellulose material and water;
   b) forming the cellulose dispersion to selected shape(s);
   c) oxidizing the cellulose dispersion with periodate;
   d) freezing the oxidized cellulose dispersion;
   e) thawing the oxidized cellulose dispersion, thereby forming a cross-linked cellulose dispersion;
   f) optionally performing a solvent exchange on the cross-linked cellulose dispersion;
   g) removing water and/or solvent from the cross-linked cellulose dispersion whilst the water and/or solvent of the dispersion is in the liquid phase, thereby providing the shape-retaining cellulose product(s),
wherein step b) is performed prior to step c), simultaneously with step c) or after step c).

2. Method according to any one of the preceding claims, wherein in step g) the water and/or solvent is removed by pressing, filtration, evaporation, or combinations thereof.

3. Method according to any one of the preceding claims, wherein step b) of forming the cellulose dispersion to selected shapes is performed by a method selected from extrusion, printing, 3D-printing, molding, embossing, emulsifying and deposition on a hydrophobic surface.

4. Method according to any one of the preceding claims, wherein if step b) is performed prior to step c) then the formed cellulose dispersion shapes are placed in an aqueous periodate bath having a periodate concentration of from about 0.5 to about 10 percent by weight.

5. Method according to any one of claims 1-3, wherein if step b) is performed simultaneously with step c) or after step c) then the periodate is blended as a powder or aqueous solution into the cellulose dispersion to provide a periodate concentration of from about 0.5 to about 10 percent, defined as dry weight periodate relative to the total weight of the cellulose dispersion.
6. Method according to any one of the preceding claims, wherein the method comprises an additional step h) after step c), wherein step h) comprises providing a particulate material and blending the particulate material with the oxidized cellulose dispersion, thereby providing a composite dispersion, wherein the particulate material is added in a quantity of from about 1 to about 80 percent, preferably from about 1 to about 60 percent, defined as the dry weight of the particulate material relative to the total dry weight of the composite dispersion.

7. Method according to claim 6, wherein the particulate material is selected from wood pulp, sawdust, ground wood, ground bark, wood fibre, rosin, polymers, polylactic acid, metals, powdered minerals, pigments, graphene, graphite, nanoparticles, nanotubes, and/or combinations thereof.

8. Method according to any one of the preceding claims, wherein the cellulose material is nanocellulose, and wherein the cellulose dispersion comprises from about 0.4 to about 10 percent of nanocellulose, defined as dry weight nanocellulose relative to the total weight of the cellulose dispersion.

9. Method according to claim 8, wherein the nanocellulose is wood- or plant-based and is chosen from cellulose nanofibrils (CNF) or cellulose nanocrystals (CNC), preferably cellulose nanofibrils.

10. Method according to any one of claims 1-7, wherein the cellulose material is wood fiber, paper pulp, regenerated cellulose, cotton, linen, abaca, coir, flax, henequen, kenaf, jute, hemp, kapok, raffia, ramie, bamboo, pina, sisal, or combinations thereof, and wherein the cellulose dispersion comprises from about 15 to about 90 percent of cellulose material, defined as dry weight cellulose material relative to the total weight of the cellulose dispersion.

11. Method according to any one of claims 1-7, wherein the cellulose material is microcrystalline cellulose, carboxymethyl cellulose, cellulose gels, or combinations thereof, and wherein the cellulose dispersion comprises from about 0.4 to about 10 percent of cellulose material, defined as dry weight cellulose material relative to the total weight of the cellulose dispersion.
12. Shape-retaining cellulose product obtained by the method of any one of the claims 1-11.

13. Nanocellulose aerogel shape(s) obtained by the method of any one of the claims 8-9.

14. Use of nanocellulose aerogel shape(s) obtained by the method of any one of the claims 8-9 as a paper additive.

15. Use of nanocellulose aerogel beads obtained by the method of any one of the claims 8-9 as a component in an ink for printing.

16. Use of nanocellulose aerogel shape(s) obtained by the method of any one of the claims 8-9 in the manufacture of textiles.

17. Use of nanocellulose aerogel shape(s) obtained by the method of any one of the claims 8-9 in energy storage applications.

18. Use of nanocellulose aerogel shape(s) obtained by the method of any one of the claims 8-9 as a chromatography or filtration media in the purification of liquids or gases.

19. Shape-retaining paper or textile obtained by the method of claim 10.
**INTERNATIONAL SEARCH REPORT**

**A. CLASSIFICATION OF SUBJECT MATTER**

**IPC:** see extra sheet

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

**IPC:** B01J, B82Y, C08B, C08J, D06M, D21H

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE, DK, FI, NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, PAJ, WPI data, BIOSIS, CHEM ABS Data, COMPENDEX, INSPEC, MEDLINE, IBM-TDB, PIRA

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

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<td>WO 2016079140 A1 (FUNDACION TECNALIA RES &amp; INNOVATION), 26 May 2016 (2016-05-26); abstract; page 3, line 17 - page 4, line 4; page 4, line 29 - page 4, line 33; page 5, line 1 - page 5, line 2; page 7, line 20 - page 7, line 27; page 12, line 8 - page 12, line 30; page 18, line 24 - page 19, line 28</td>
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Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents:
  *A* document defining the general state of the art which is not considered to be of particular relevance
  *E* earlier application or patent but published on or after the international filing date
  *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
  *O* document referring to an oral disclosure, use, exhibition or other means
  *P* document published prior to the international filing date but later than the priority date claimed

**Date of the actual completion of the international search**

18-05-2017

**Date of mailing of the international search report**

18-05-2017

**Name and mailing address of the ISA/SE**
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**Authorized officer**
Kristin Persson

**Telephone No.** +46 8 782 28 00

Form PCT/ISA/210 (second sheet) (January 2015)
### DOCUMENTS CONSIDERED TO BE RELEVANT

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<td>WO 201 1088889 A1 (SOEDRA SKOGSAEGARNA EKONOMISK FOERENING ET AL), 28 July 2011 (201 1-07-28); abstract; page 5, line 17 - page 5, line 27; claims 1-2,16</td>
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<td>WO 201401 1112 A1 (CELLUTECH AB), 16 January 2014 (2014-01-16); abstract; claims 1,6</td>
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<td>A</td>
<td>LU, T. et al. 'Composite aerogels based on dialdehyde nanocellulose and collagen for potential applications as wound dressing and tissue engineering scaffold' In: Composites Science and Technology, 2014, Vol. 94, pp. 132-138; abstract; page 133</td>
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<td>YANG, X. et al. 'Chemically cross-linked cellulose nanocrystal aerogels with shape recovery and superabsorbent properties' In: Chemistry of materials, 2014, Vol. 26, pp. 601 6-6025; abstract; pages 601 7-601 8</td>
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International Patent Classification (IPC)

- **C08J 9/28** (2006.01)
- **B01J 13/00** (2006.01)
- **C08B 15/10** (2006.01)
- **B82Y 30/00** (2011.01)
- **C08J 9/35** (2006.01)
- **D21H 11/18** (2006.01)
- **D21H 21/52** (2006.01)
### International Search Report

**Information on patent family members**

**PCT/SE2017/050221**

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